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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Marc-Andre Theoleyre
Appl. No. : 10/526,827
Filed : April 22, 2005
For : METHOD FOR DECALCIFICATION OF AN AQUEOUS SOLUTION,
IN PARTICULAR OF LACTOSERUM OR OF AN ULTRAFILTRATION
PERMEATE OF LACTOSERUM

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION OF STANISLAS BAUDOUIN

Sirs:

I, Stanislas Baudouin declare and state as follows:

1. I am a citizen of France and a resident of the city of Perigny, 17180
2. I have been graduated as chemical Engineer
3. I was R&D chromatography specialist of Applexion from 1998 to 2008.

My professional responsibilities included, development of new processes involving ion exchange resins, chromatography and membranes separations.

4. I have reviewed the above-identified Application No. 10/526,827 of April 22, 2005, entitled "a method for decalcification of an aqueous solution, in particular of lactoserum or of an ultrafiltration permeate of lactoserum", hereinafter "the subject application".

5. I am making this Declaration in support of the amended claims of the application identified in paragraph 4, above.

6. I have read and understood the disclosure of the prosecution history of the subject application.

7. At the time of filing the present application, there was a need in the dairy industry to find efficient methods to remove Ca^{2+} and Mg^{2+} ions. In lactose crystallization processes using whey, a calcium phosphate precipitation occurs during the evaporation and crystallization steps. In order to avoid the formation of calcium phosphate which bothers the heat exchange, softening the whey is necessary. Moreover when lactose is recovered from whey by chromatographic process, Ca^{2+} must be removed prior to that operation. Several techniques have been used in the past to eliminate the Ca^{2+} and Mg^{2+} ions. Good results were obtained in the sugar industry.

8. One of the known methods in the sugar refinery industry, consists in using strong cationic resins. Ca^{2+} and Mg^{2+} ions were exchanged with Na^+ or K^+ ions. Surprisingly, this method was found difficult for softening whey, due to the formation of complexes between the Ca^{2+} and Mg^{2+} ions and the conjugate base of some acids. These complexes make the Ca^{2+} and Mg^{2+} less available for an exchange and result in a loss of yield.

9. Another known method consists in using a weak cationic resin, which has more affinity with the Ca^{2+} and Mg^{2+} ions. But the regeneration of the resin is costly when the counter ion is Na^+ or K^+ , because it requires a first step in which Ca^{2+} and Mg^{2+} are replaced by H^+ , then a second step in which H^+ is replaced by Na^+ or K^+ .

10. Therefore there was a need for a method for removing the Ca^{2+} and Mg^{2+} ions from the dairy solutions which would overcome the disadvantages associated with practicing the previously known methods in the sugar industry.

11. Surprisingly, it has been found that the use of an anionic resin with a monovalent anion as the counter ion and then the use of a cationic resin with a monovalent metal cation as the counter ion are much more efficient than the use of a cationic resin on its own.

12. The exchange of the divalent anions by monovalent anions like chloride before the cations exchange improves the availability of the $\text{Ca}^{2+}/\text{Mg}^{2+}$ and thus improves the efficiency of the cationic resin.

13. The following strong cationic resins and strong anionic resin have been used in comparative tests:

Name	IRA 458	SR1L Na	252 Na
Type	AF	CF	CF
	Gel	Gel	Macroporous
	Acrylic	Styrenic	Styrenic
DVB		8	12
Capacity (eq/l)	1.25	2.05	1.80
Density	1.08	1.28	1.22

AF: strong Anionic exchanger

CF: strong Cationic exchanger

14. The following raw materials have been used for the experiments:

<i>Product</i>	Brix	pH	Cond.	Turbidity	Ca+Mg*	Na+K*
Unity	(%)		(mS/cm)	(Icumsa)	(meq/l)	(meq/l)
Whey permeate	5.7	6.3	5.3	2490	25	52.4
Mother liquor	28.2	4.94	30.4	6428	144	868

* data provided by the supplier.

15. The table below shows comparative results for the softening of the whey permeate using a strong cationic resin SR1L Na (tests 1-2) or the combination of a strong anionic resin before a strong cationic resin IRA 458 - SR1L Na (tests 3-4).

Test / V res	Vol feed	Ca in	Loading	Capacity	Softening	Regenerant	Rege level
No./ml	BV	meq/l	eq/l _{res}	eq/l _{res}	%		eq/l _{res}
1 / 125	25	26,5	0,66	0,49	73,6	mother liquor	1,7
2 / 125	25	26,5	0,66	0,48	72,8	KCl + NaCl	2,5
3 / 125	25	24,0	0,60	0,57	95,0	KCl + NaCl	2,5
4 / 125	25	26,5	0,66	0,65	97,7	mother liquor	1,7

16. By comparing experiments with equivalent conditions, it can be seen that removal of anions on an anionic resin prior to the softening step improves that last step.

17. Test No. 2 and 3 (Regenerant = KCl + NaCl, with a concentration (K + Na) = 1,2 eq/l and a ratio K/Na = 60/40)

The softening rate is 72,8% using the strong cationic resin and 95,0% using a strong anionic resin before this step. Moreover, the capacity of the resin is improved (0,48 to 0,57 eq/l_{res}).

18. Tests No. 1 and 4 (Regenerant = mother liquor)

The softening rate is 73,6% using the strong cationic resin and 97,7% using a strong anionic resin before this step. Moreover, the capacity of the resin is improved (0,49 to 0,65 eq/l_{res}).

19. The Table below shows the test results obtained by comparing a strong cationic resin, two strong cationic resins and a strong anionic resin prior to a strong cationic resin in equivalent conditions (V_{res} = 125 mL, Loading = about 0,8 eq/l_{res}).

Raw material	System	Capacity (eq/lres)	Softening (%)
Sweet whey permeate	CF	0.7	88
Sweet whey permeate	CF-CF	0.7	95
Sweet whey permeate	AF-CF	0.8	95
Acid whey	CF	0.9	83

20. It can be seen that the use of a strong anionic resin prior to a strong cationic resin ("AF-CF" system) shows the best results : the softening rate is 95% and is improved in comparison with the use of a cationic resin on its own (88% starting from sweet whey permeate; 83% starting from acid whey).

21. The softening rate is similar to the use of two cationic resins ("CF-CF" system). However, the capacity of the resin is improved (0,8 eq/lres).

22. Therefore the "AF-CF" system shows much better overall results than the "CF-CF" system.

23. Thus, the order of the elution steps has indeed an importance.

24. No test was performed using a "CF-AF" system since the results would be at best similar to the "CF-CF" system, in which no anionic resin is used before the cationic resin.

25. These tests above all demonstrate that in whey permeate the calcium is less available for exchange due to the presence of some anion (PO_4 or weak organic bases). Removal of these anions on an anionic resin prior to the softening improves that last step of the process.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 US Code 1001, and that

such willful false statement may jeopardize the validity of this application or any patent issuing thereon.

Dated:

Stanislas Baudouin

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Dated: June 25, 2009

Stanislas Baudouin

